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(54) ALUMINUM-CHROMIUM ALLOY AND PRODUCTION THEREOF

ALUMINIUM-CHROM-LEGIERUNG UND VERFAHREN ZUR HERSTELLUNG

ALLIAGE D'ALUMINIUM ET DE CHROME ET PRODUCTION DE CET ALLIAGE

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Description

SPECIFICATION

5 Title of the Invention

Aluminum-Chromium Based Alloy and Method of Preparing the Same

10 Field of the Invention

The present invention relates to an aluminum-chromium based alloy and a method of preparing the same, and more particularly, it relates to an aluminum-chromium based alloy which has high strength and is excellent in heat resistance, corrosion resistance and the like, and a method of preparing the same.

15 Background of the Invention

Amorphous aluminum alloys are disclosed in Japanese Patent Laying-Open Gazette No. 1-275732, Japanese Patent Publication Gazette No. 64-47831 and Japanese Patent Publication Gazette No. 1-127641, for example. The amorphous aluminum alloys disclosed in these gazettes contain La, or Nb, Ta, Hf, Y and the like as essential alloy contents. An Al-Si-X alloy and an Al-Ce-X alloy are described in Transactions of the Japan Institute of Metals, Vol. 28, No. 12, p. 968.

The amorphous alloys disclosed in the aforementioned prior art examples are prepared by a super-rapid solidification method in most cases. As to another method, it is said that an amorphous alloy can be prepared also by a mechanical alloying method. In addition to the aforementioned two methods, a vapor phase deposition method, an electrolytic deposition method, an electron beam irradiation method, an extra-high pressure method and the like are known as methods for obtaining amorphous alloys. However, these methods have not yet been industrialized due to considerable restriction in practice.

An amorphous alloy prepared by the super-rapid solidification method or the mechanical alloying method has not satisfied both mechanical and economical properties. In other words, an amorphous alloy having excellent mechanical properties contains high-priced elements. An amorphous alloy containing only low-priced elements has inferior mechanical properties. An amorphous alloy is crystallized by heating. If the crystallization temperature of the amorphous alloy is too low, it is impossible to perform sufficient warm solidification of alloy powder. Also in view of actual employment, it is difficult to use such an amorphous alloy having a low crystallization temperature since the upper limit of available temperatures is lowered.

JP-A-63-153 237 discloses an Al-based alloy partly having an amorphous structure, said alloy comprising as additional elements at least one out of Cr, Mn, Fe, Co and Ni in an amount of 4 to 23 atomic percent as well as Si or Ge in an amount of 8 to 54 atomic percent, the additional elements not exceeding 67 atomic percent.

An object of the present invention is to provide an aluminum-chromium based alloy which can satisfied both mechanical and economical properties.

Another object of the present invention is to provide an aluminum-chromium based alloy which has a high crystallization temperature.

Still another object of the present invention is to provide a method of preparing an aluminum-chromium based alloy which can satisfy both mechanical and economical properties.

A further object of the present invention is to provide a method of preparing an aluminum-chromium based alloy which has a high crystallization temperature.

The inventors have found that an aluminum-chromium based alloy containing an amorphous phase can be obtained by preparing an Al-Cr-X based alloy by a novel method. They have further found that the above described aluminum-chromium based alloy containing an amorphous phase has a high crystallization temperature, and is excellent in material characteristics. Such an Al-Cr-X based alloy is also excellent in economical property since low-priced Cr is employed as a raw material.

An attempt for obtaining an Al-Cr amorphous alloy is disclosed in Transactions of the Japan Institute of Metals, Vol. 28, No. 8 (1987), p. 679, for example. While a vapor-phase method, i.e., an RF sputtering method, is employed in this prior art, only a quasi-crystalline structure, which is thermodynamically more stable than an amorphous phase, is obtained by this method. In general, it has been recognized that absolutely no amorphous phase is obtained in an Al-Cr based alloy even if a super-rapid solidification method or a mechanical alloying method is employed.

As described above, it has been difficult to convert an Al-Cr based alloy to an amorphous state. In order to implement such amorphous conversion of an Al-Cr based alloy, the inventors have attached importance to the following two points:

- (1) Additional element groups for facilitating amorphous conversion and a novel alloy composition.
- (2) A novel preparation method including a novel thermomechanical working treatment method implementing conversion to an amorphous state.

In order to obtain an Al-Cr based amorphous alloy, combination of such novel alloy composition and novel preparation method is indispensable.

An aluminum-chromium based alloy according to the present invention contains 10 to 25 atomic percent of Cr, and 0.1 to 5.0 atomic percent of at least one element selected from a group of Fe and Ni and optionally not more than 30 atomic percent of at least one element selected from Ti, Zr, Si, V, Nb, Mo, W, Mn, Co and Hf. The total content of Cr, and Fe and/or Ni is not more than 30 atomic percent. The rest, apart from impurities, consists of aluminum. This aluminum-chromium based alloy partially or entirely exhibits an amorphous structure by X-ray diffraction or electron beam diffraction. It contains second phase reinforcing materials such as particles, whiskers and short fibers in dispersed states.

The aforementioned aluminum-chromium based alloy is prepared by the following method:

In one aspect, the method of preparing an aluminum-chromium based alloy comprises a step of obtaining a foil or powder raw material from a melt by a rapid solidification method, a step of obtaining powder, which is converted to an amorphous state, by performing a mechanical grinding treatment or a mechanical working treatment equivalent thereto on the raw material, and a step of performing warm solidification of the amorphous powder.

In another aspect, the method of preparing an aluminum-chromium based alloy comprises a step of obtaining aluminum-chromium binary system alloy powder from a melt of an aluminum-chromium binary system alloy by a rapid solidification method, and a step of alloying remaining elements other than aluminum and chromium in the aluminum-chromium binary system alloy powder by a mechanical alloying method.

In still another aspect, the method of preparing an aluminum-chromium based alloy comprises a step of obtaining crystalline powder by alloying industrial pure aluminum powder, pure chromium or an aluminum mother alloy containing chromium, and remaining elements other than aluminum and chromium or mother alloys of the elements by a mechanical alloying method, a step of partially or entirely converting the crystalline powder to an amorphous state by a thermal activation annealing treatment, and a step of performing warm solidification of the amorphous powder. Preferred manufacturing methods are disclosed in the dependent claims 3 and 4, 6 and 8 to 10.

The additional element groups described in the item (1) are adapted to facilitate formation of an amorphous phase when an aluminum-chromium based alloy is prepared by the method described in the item (2). In particular, it is conceivable that Fe and Ni of the first group are essential elements for converting the aluminum-chromium based alloy to an amorphous state. Ti, Zr, Si, V, Nb, Mo, W, Mn, Co and Hf of the second group are elements for improving various characteristics of the alloy without much inhibiting amorphous conversion of the aluminum-chromium based alloy.

While no clarification has been made as to what metallurgical action the elements of the first group have on the aluminum-chromium based alloy, it is conceivable that presence of Fe and Ni hinders immediate transition from a simply mixed state, which is thermodynamically most instable, or a supercooled liquid, which is in a next instable state, to a crystalline phase, which is an equilibrium stable phase, and provides an opportunity for remaining in a metastable amorphous phase. The upper limit of the content of the first group elements is 5 atomic percent, since amorphous conversion may be hindered if the content exceeds this limit. The lower limit of the content of the first group elements is 0.1 atomic percent, since no effect of amorphous conversion is attained if the content is less than this limit.

In consideration of relation between the first group element(s) of Fe and/or Ni and Al-Cr, which are basic alloys, a preferable content of Cr is 10 to 25 atomic percent. If the content of Cr is not more than 10 atomic percent, mechanical properties of the aluminum-chromium based alloy are deteriorated and amorphous conversion is hard to occur. If the Cr content exceeds 25 atomic percent, lightweightness is damaged and characteristics for serving as a practical material are also deteriorated in view of toughness and the like. Further, amorphous conversion is hard to occur.

In order to facilitate amorphous conversion without damaging lightweightness of the aluminum-chromium based alloy, the total content of Cr, and Fe and/or Ni must be not more than 30 atomic percent.

While relation between the function of the second group elements consisting of Ti, Zr, Si, V, Nb, Mo, W, Mn, Co and Hf and the mechanism of amorphous conversion is not clear, an effect of improving physical, chemical or mechanical properties of the aluminum-chromium based alloy without hindering amorphous conversion is attained upon addition of the second group elements. If the content of the second group elements exceeds 30 atomic percent, however, original characteristics of the Al-Cr based alloy are damaged.

There is not necessarily a fixed criterion as to verification of an amorphous material. X-ray diffraction is the simplest method for deciding whether or not a material is amorphous. When a prepared alloy is subjected to X-ray diffraction, a sharp diffraction peak appears from a crystal plane if the alloy is crystalline. If no such sharp diffraction peak appears but something like a trace of an extremely spread diffraction peak is recognized, it is possible to decide that the material is macroscopically amorphous.

Electron beam diffraction is a method for more macroscopically confirming presence of an amorphous phase. When a structure specified by observation with a transmission electron microscope is diffracted with electron beams, it is

possible to decide this structure as being amorphous if the so-called halo pattern, which is not recognized in a crystalline material, vaguely appears with appearance of no regular diffraction line nor diffraction point group.

In addition to X-ray diffraction and electron beam diffraction, there is still another method for deciding whether or not a material is amorphous. For example, DSC (differential scanning calorimeter) analysis is adapted to decide whether or not a material has been amorphous with exothermic reaction in crystallization by heating. However, this analysis method is not suitable for state analysis of the inventive alloy since it requires heating. In the DSC analysis, further, it is difficult to make a correct decision when a part of the material is amorphous and the rest is crystalline. On the other hand, an amorphous phase can be identified by electron beam diffraction with extremely good sensitivity since it is possible to specify the structure in nanometer units.

Thus, the essential condition of the present invention has been set in that the aluminum-chromium based alloy has an amorphous structure which is identified by X-ray diffraction or electron beam diffraction.

A method of preparing an amorphous phase according to the present invention is different from conventional methods, and classified into the following two methods. It is possible to obtain an amorphous phase by either method.

The first method is adapted to produce an amorphous phase by performing a mechanical grinding treatment on powder or foil which is obtained by a rapid solidification method. The rapid solidification method has frequently been used as a method of obtaining an amorphous phase. As to an Al-Cr based alloy, however, only a quasi-crystalline phase, which is close to an amorphous phase, has been obtained even if the same was rapidly solidified under the best conditions. The inventors have found that it is possible to thermodynamically convert this quasi-crystalline phase to an amorphous phase by mechanically grinding the same. The material may not necessarily have a quasi-crystalline structure before the same is subjected to a mechanical grinding treatment. However, it is preferable to obtain the material to be subjected to mechanical grinding treatment by the rapid solidification method. According to the rapid solidification method, it is possible to implement such a state that Al atoms and Cr atoms, which are principal elements, are homogeneously mixed as primitively as possible without forming coarse intermetallic compounds or the like.

Throughout this specification, rapid solidification means that the solidification rate is at least 10^3 K/sec., which is a solidification rate attained by a general atomizing method, a splat cooling method or the like. With increase of the solidification rate, the solidified structure of the Al-Cr based alloy is refined and supersaturated dissolution of elements such as Cr in Al progresses to cause refinement of intermetallic compounds, and finally a quasi-crystalline structure starts to appear, so that the entire alloy enters a quasi-crystalline state in the end. Amorphous conversion by mechanical grinding is facilitated with increase of the solidification rate. This is because the thermodynamic state of an intermediate product gradually approaches the state of an amorphous phase with increase of the solidification rate.

The inventors have found that a remarkable effect is attained by performing mechanical grinding in an Al-Cr based alloy. Namely, milling, mixing and adhesion/aggregation of powder are repeated by mechanical working so that the interior of the powder is homogeneously mixed not only in macroscopic units but also in atomic units and thermodynamically activated into an extremely instable state by increase of grain boundary energy caused by refinement and lamination as the result, and phase transition from such an instable state to a metastable amorphous phase is further enabled.

In the aforementioned first method, the first group elements and/or the second group elements may be added in rapid solidification or in mechanical grinding. The first group elements are preferably added in mechanical grinding since it is easier to add the same in mechanical grinding than in rapid solidification. It is also preferable to add a high-melting point element or an oxidizable element in mechanical grinding, in order to avoid a problem of dissolution.

Difference between mechanical alloying (MA) and mechanical grinding (MG) is now described.

Mechanical alloying is a treatment which is adapted to perform complex working processes such as mechanical mixing, pulverization and aggregation on at least one type of raw material powder containing elements for forming the composition of the target alloy so that individual particles have the target alloy composition as well as microscopically homogeneous structures.

On the other hand, mechanical grinding is a treatment which is adapted to perform complex working processes such as mechanical working, pulverization and aggregation on alloy powder having the composition of the target alloy, thereby introducing distortion, lattice defects etc. into the alloy powder. While mechanical alloying changes the alloy components of the powder, mechanical grinding is not mainly directed to change the alloy components. Although contamination of unavoidable impurities may be caused also in mechanical grinding, such contamination is not a principal object.

Comparing mechanical alloying and mechanical grinding with each other, these treatments have different starting raw materials. As to actual operations, however, these treatments can be performed with absolutely identical apparatuses and conditions. For example, a high-energy ball mill called an attriter, a general ball mill, a planetary ball mill, a vibrating mill, a centrifugal mill (angmill) or the like may be employed for both mechanical alloying and mechanical grinding.

In the second method according to the present invention, the final composition alloy is not obtained through a dissolution step. Namely, the second method according to the present invention is a novel method of obtaining an amorphous phase, which cannot be obtained by mechanical alloying alone, by preparing crystalline powder which is microscopically and atomically homogeneously mixed as an intermediate raw material by mechanical alloying and thereafter

performing a thermal activation annealing treatment on this powder. Although it is known that an amorphous phase can be produced by mechanical alloying alone depending on alloy components, the composition range thereof is extremely restricted.

When an amorphous phase is heated, the same is ready for transition to a crystalline phase, which is an essentially stable system. Therefore, conversion of a material, which is not yet in an amorphous state after mechanical alloying, to an amorphous state by heating is absolutely innovative recognition against common sense. It is already known that forced solid solution and compounding in nanometer units can be implemented by mechanical alloying. After an alloy having the inventive composition is subjected to mechanical alloying, its structure is not an amorphous phase but a crystalline phase. This crystalline phase, which is a mixture of a compound group having compositions displaced from those of stoichiometric compounds, is in a thermodynamically high free energy state as compared with a stable stoichiometric compound having the lowest thermodynamic free energy, and at a level slightly higher than the free energy level of an amorphous phase. Thus, the inventors have found that it is possible to slightly reduce the free energy level of such a crystalline phase to convert the same to a metastable amorphous phase by performing a thermal activation annealing treatment after mechanical alloying.

In order to obtain a homogeneous intermediate raw material, it is necessary to use industrial pure aluminum powder, pure chromium or an aluminum mother alloy containing chromium, and other alloying elements or mother alloys of these elements. In mechanical alloying, which indispensably requires appropriate balance between cold welding, i.e., seizureability, and crushing/dispersion of hard brittle powder, combination of the aforementioned raw materials is important.

The thermal activation annealing treatment may be performed during a warm solidification process, or independently of such a warm solidification process. It is preferable to perform the thermal activation annealing treatment in the powder state in view of a further homogeneous treatment, while the thermal activation annealing treatment is preferably performed during the warm solidification process in view of the economical property. In either case, it is necessary for this thermal activation annealing treatment to set an optimum temperature in a temperature range of 400 to 800 K as well as to select an optimum holding time, in response to the alloy to be treated.

According to either one of the aforementioned first and second methods, it is possible to obtain an amorphous phase. Either method may be arbitrarily selected. It is preferable to select either method in response to easiness of preparation of the raw material powder as well as preparation of the intermediate raw material powder. In the case of an alloy which is hard to dissolve, for example, it is preferable to obtain alloy powder having a desired composition by preparing the powder not by a rapid solidification method but by a mechanical alloying method. When an extremely long time is required for homogenization or a composition is oxidized by mechanical alloying, or a quasi-crystalline structure is obtained by rapid solidification, it is preferable to prepare alloy powder by rapid solidification. In either method, 500 to 5000 p.p.m. of oxygen is unavoidably contained. While it has not yet been clarified as to whether or not the contained oxygen contributes to formation of the amorphous phase, there is no evidence which is deniable of such contribution.

As to a powder solidification method of the present invention, it is possible to employ warm powder extrusion, powder welding, powder forging or the like, which has been used in general. More preferably, a warm solidification treatment is performed at a temperature which is higher than the glass transition point of the amorphous phase and lower than its crystallization temperature, in view of characteristics of the amorphous phase. When the treatment is performed under this temperature condition, glass fluidity is utilized and it is possible to effectively solidify/form the powder into a precise/complicated configuration.

The aluminum-chromium based alloy may be used as a matrix, to contain second phase reinforcing materials such as particles, whiskers and short fibers in dispersed states. An aluminum-chromium based alloy containing a reinforcing dispersed layer will have more excellent composite functions. In this case, it is possible to improve strength of boundary by performing compounding through solidification utilizing glass fluidization, in particular.

Brief Description of the Drawings

Figs. 1A and 1B are typical diagrams showing free energy levels of binary system based alloys at arbitrary temperatures TK.

Fig. 2 shows X-ray photographs showing the crystal structure of Al-15%Cr powder which was annealed at 740 K after the same was subjected to mechanical alloying for 1000 hours.

Fig. 3 shows an X-ray diffraction pattern of Al-15%Cr powder which was annealed at 740 K and 920 K after the same was subjected to mechanical alloying for 1000 hours.

Fig. 4 is an X-ray diffraction pattern of pulverized powder of rapidly solidified Al-20at.%Cr foil, which was subjected to mechanical grinding for 300 hours, around heating.

Fig. 5 is a DSC (differential scanning calorimeter) analysis diagram of pulverized powder of rapidly solidified Al-20at.%Cr foil, which was subjected to mechanical grinding, in continuous heating.

Examples

The following treatments A1 to C5 were performed on raw materials having blending/compositions shown in Table 1. Table 2 shows the processes and characteristics of the as-obtained alloys. The contents of the processes described in the columns of steps 1 and 2 in Table 2 are as follows:

A1: preparation of powder by atomizing method using inert gas - treatment by ball mill filled with argon gas (100 hours)

A2: preparation of powder by atomizing method using inert gas - mechanical alloying (attriter - 50 hours)

A3: preparation of foil member by quench single roll method - ball mill pulverization and ball mill mechanical grinding (1000 hours)

B1: mechanical alloying (attriter - 50 hours) ... thermal activation annealing (700 K, 10 hours)

C1: CIP forming ... degassing ... filling into can ... extrusion (673 K, 1:10 in extrusion ratio, 8 mm in diameter)

C2: lubrication of metallic mold ... cold forming (5 ton/cm²) ... heating in inert gas (700 K, 20 minutes) ... warm forging ... re-sintering (700 K, 1 hour)

C3: lubrication of metallic mold ... cold forming (5 ton/cm²) ... thermal activation annealing in inert gas (700 K, 5 hours) ... preheating for forging (673 K, 20 minutes) ... warm forging ... re-sintering (700 K, 1 hour)

C4: lubrication of metallic mold ... cold forming ... heating in inert gas (800 K, 30 minutes) ... glass fluidization forming/solidification

C5: mixing of reinforcing material ... lubrication of metallic mold ... cold forming (5 ton/cm²) ... heating in inert gas (800 K, 30 minutes) ... glass fluidization forming/solidification

Table 1

Composition	Cr	Ni	Fe	Other Element 1	Other Element 2	Al
X1	5	0.4	3			bal
X2	10	0.4	3			bal
X3	15	0.4	3			bal
X4	20	0.4	3			bal
X5	25	0.4	3			bal
X6	30	0.4	3			bal
Y1	15	0	0			bal
Y2	15	6	3			bal
Y3	15	3	6			bal
Y4	15	0.4	3			bal
Z1	20	0.4	3	Ti-5	V-0.25	bal
Z2	20	0.4	3	Zr-1	Mo-2	bal
Z3	20	0.4	3	Nb-3	Hf-1	bal
Z4	20	0.4	3	Si-8	W-2	bal
Z5	20	0.4	3	Mn-3	Co-1	bal
W1	15	0.4	3	SiC-Whisker-10		bal
W2	15	0.4	3	SiC-Powder-10		bal
W3	15	0.4	3	C Short Fiber-10		bal

Table 2

No.	Composition	Step 1	Step 2	Phase	Invention	Room Temperature Strength (kg/mm ²)	Anneal Strength (kg/mm ²) After Annealing at 450°C for 100h.	Corrosion Resistance After Salt Spray Test
1	X1	A3		crystalline	NO			
2	X2	A3		amorphous	YES			
3	X3	A3		amorphous	YES			
4	X4	A3		amorphous	YES			
5	X5	A3		amorphous	YES			
6	X6	A3		crystalline	NO			
7	Y1	A2		crystalline	NO			
8	Y2	A2		crystalline	NO			
9	Y3	A2		crystalline	NO			
10	Y4	A2		amorphous	YES			
11	X3	A1		amorphous	YES			
12	Y4	B1		amorphous	YES			
13	Z1	A2		amorphous	YES			
14	Z2	A2		amorphous	YES			
15	Z3	A2		amorphous	YES			
16	Z4	A2		amorphous	YES			
17	Z5	A2		amorphous	YES			
18	X3	A1	C1	amorphous	YES	85	84	no rusting
19	X3	A1	C2	amorphous	YES	82	82	
20	X3	B1	C3	amorphous	YES	81	81	
21	X3	A1	C4	amorphous	YES	87	86	
22	W1	A1	C5	amorphous	YES	90	90	

Continuation of the Table on the next page

Table 2 (continued)

No.	Composition	Step 1	Step 2	Phase	Invention	Room Temperature Strength (kg/mm ²)	Anneal Strength (kg/mm ²) After Annealing at 450°C for 100h.	Corrosion Resistance After Salt Spray Test
23	W2	A1	C5	amorphous	YES	85	85	
24	W3	A1	C5	amorphous	YES	86	86	

While abrupt deterioration of characteristics has been recognized in a conventional amorphous alloy following local or instantaneous temperature rise, it is possible to prevent such abrupt deterioration of characteristics following temperature rise in the inventive amorphous alloy since the amorphous state can be maintained up to an extremely high temperature, as clearly understood from Fig. 5. Further, the inventive amorphous alloy has characteristics which are further excellent as compared with those of a conventional crystalline type aluminum-transition element dispersion-strengthened heat resisting alloy.

Then, refer to Figs. 1A and 1B showing free energy levels of binary system alloys. When the first method of the present invention is employed, quasi-crystals etc. are activated from a level of C_4 to a C_2 level by mechanical grinding, and thereafter converted to a C_3 level. When the second method of the present invention is employed, the same enter the C_1 to C_2 levels in a mechanical alloying state, and converted to the C_3 level by subsequent heating. In practice, the levels of C_1 to C_2 are present as the result of a mixture of non-stoichiometric compounds ($A_{n-x}B_{m+x}$) of crystalline materials having displaced compositions of C_6 and C_7 , and the composition of A_nB_m is changed and distributed as $A_{n-x}B_{m+x}$ in a partial view. Referring to Fig. 1B, the peak of the higher temperature side shows transition from the C_3 level to the C_5 level, i.e., energy release following crystallization.

X-ray photographs of Fig. 2 show the crystal structure of Al-15%Cr powder, which was subjected to mechanical alloying for 1000 hours and thereafter annealed at 740 K. Fig. 3 shows an X-ray diffraction diagram of Al-15%Cr powder, which was subjected to mechanical alloying for 1000 hours and thereafter annealed at 740 K and 920 K. Fig. 4 shows an X-ray diffraction diagram of pulverized powder of rapidly solidified Al-20at.%Cr foil, which was subjected to mechanical grinding for 30 hours, around heating. Fig. 5 shows a DSC (scanning differential thermal capacity) analysis diagram of pulverized powder of rapidly solidified Al-20at.%Cr foil, which was subjected to mechanical grinding for each time, in continuous heating.

Industrial Availability

The aluminum-chromium based alloy according to the present invention, which has strength, heat resistance and wear resistance of iron and steel materials and light weightness of an aluminum alloy as well as corrosion resistance of an amorphous alloy, is applicable to various uses such as an automobile, a domestic electric apparatus, an industrial apparatus, an aircraft, an electronic apparatus, a chemical apparatus, and the like.

Claims

1. An aluminum-chromium based alloy containing 10 to 25 atomic percent of Cr, optionally not more than 30 atomic percent of at least one element selected from Ti, Zr, Si, V, Nb, Mo, W, Mn, Co and Hf, and 0.1 to 5.0 atomic percent of at least one element selected from a group of Fe and Ni, wherein

the total content of said Cr, and said Fe and/or Ni is not more than 30 atomic percent, and the rest, apart from impurities, consists of aluminum, said aluminum-chromium based alloy partially or entirely exhibiting an amorphous structure by X-ray diffraction or electron beam diffraction, characterized in that second phase reinforcing materials such as particles, whiskers and short fibers are contained in dispersed states.

2. A method of preparing an aluminum-chromium based alloy according to claim 1 said method comprising:

a step of obtaining a foil or powder raw material from a melt by a rapid solidification method, a step of obtaining powder, being converted to an amorphous state, by performing a mechanical grinding treatment or a mechanical working treatment equivalent thereto on said raw material, and a step of performing warm solidification of said amorphous powder.

3. A method of preparing an aluminum-chromium based alloy in accordance with claim 2, wherein said raw material powder obtained by said rapid solidification method partially has a quasi-crystalline structure.

4. A method of preparing an aluminum-chromium based alloy in accordance with claim 2 or 3, wherein said warm solidification treatment is performed at a temperature being higher than the glass transition point of said amorphous phase and lower than its crystallization temperature.

5. A method of preparing an aluminum-chromium based alloy, according to claim 1 said method comprising:

a step of obtaining aluminum-chromium binary system alloy powder from a melt of an aluminum-chromium binary system alloy by a rapid solidification method, and a step of alloying remaining elements other than aluminum and chromium in said aluminum-chromium binary system alloy powder by a mechanical alloying method.

- 5 6. A method of preparing an aluminum-chromium based alloy in accordance with claim 5, wherein said aluminum-chromium binary system alloy powder obtained by said rapid solidification method partially or entirely has a quasi-crystalline structure.
- 10 7. A method of preparing an aluminum-chromium based alloy, according to claim 1 said method comprising:
a step of obtaining crystalline powder by alloying industrial pure aluminum powder, pure chromium or an aluminum mother alloy containing chromium, and remaining elements other than aluminum and chromium or mother alloys of said elements by a mechanical alloying method,
15 a step of partially or entirely converting said crystalline powder to an amorphous state by a thermal activation annealing treatment, and
a step of performing warm solidification of said amorphous powder.
- 20 8. A method of preparing an aluminum-chromium based alloy in accordance with claim 7, wherein said amorphous conversion step and said warm solidification step are simultaneously carried out.
9. A method of preparing an aluminum-chromium based alloy in accordance with claim 7 or 8, wherein said thermal activation annealing treatment is performed in a temperature range of 400 to 800 K.
- 25 10. A method of preparing an aluminum-chromium based alloy in accordance with claim 7, 8 or 9, wherein said warm solidification treatment is performed at a temperature being higher than the glass transition point of said amorphous phase and lower than its crystallization temperature.

Patentansprüche

- 30 1. Auf Aluminium-Chrom basierende Legierung, welche enthält:
10 bis 25 Atom-% Cr,
eventuell nicht mehr als 30 Atom-% von mindestens einem Element, ausgewählt aus Ti, Zr, Si, V, Nb, Mo, W,
35 Mn, Co und Hf, und
0,1 bis 5,0 Atom-% von mindestens einem Element ausgewählt aus einer Gruppe aus Fe und Ni, worin der Gesamtgehalt an Cr, und Fe und/oder Ni nicht mehr als 30 Atom-% ist, und
der Rest, abgesehen von Unreinheiten, aus Aluminium besteht, wobei die auf Aluminium-Chrom basierende Legierung teilweise oder vollständig eine amorphe Struktur bei Röntgenbeugung oder Elektronenbeugung
40 zeigt, **gekennzeichnet dadurch, daß**
zweitphasen-Verstärkungsmaterialien wie Partikel, Metallspitzen und kurze Fasern in dispersen Zustand enthalten sind.
- 45 2. Verfahren zur Herstellung einer auf Aluminium-Chrom basierende Legierung nach Anspruch 1, wobei dieses Verfahren umfaßt:
einen Schritt zum Erhalten eines Folien- oder Pulverrohmaterials aus einer Schmelze durch ein Schnellerstarungsverfahren,
einen Schritt zum Erhalten eines Pulvers, welches durch Ausführen einer mechanischen Zermahlungsbehandlung oder einer mechanischen Bearbeitungsbehandlung ähnlich zu derjenigen beim Rohmaterialpulver in einen amorphen Zustand umgewandelt wird, und
einen Schritt zum Ausführen einer Warmerstarrung des amorphen Pulvers.
- 50 3. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 2, worin das Rohmaterialpulver, welches durch das Schnellerstarungsverfahren erhalten wurde, teilweise eine quasi-kristalline Struktur hat.
- 55 4. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 2 oder 3, worin die

Warmerstarrungsbehandlung bei einer Temperatur ausgeführt wird, die höher als der Glasübergangspunkt der amorphen Phase und niedriger als ihre Kristallisationstemperatur ist.

5. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 1, wobei das Verfahren umfaßt:

einen Schritt zum Erhalten eines Aluminium-Chrom-Zweistoffsystem-Legierungspulvers aus einer Schmelze einer Aluminium-Chrom-Zweistoffsystem-Legierung durch ein Schnellerstarrungsverfahren, und einen Schritt zum Legieren der verbleibenden Elemente außer Aluminium und Chrom in dem Aluminium-Chrom-Zweistoffsystem-Legierungspulver durch ein mechanisches Legierungsverfahren.

6. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 5, worin das Aluminium-Chrom-Zweistoffsystem-Legierungspulver, welches durch ein Schnellerstarrungsverfahren erhalten wird, teilweise oder vollständig eine quasi-kristalline Struktur hat.

7. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 1, wobei das Verfahren umfaßt:

einen Schritt zum Erhalten eines kristallinen Pulvers durch Legieren von industriell reinem Aluminiumpulver, reinem Chrom oder einer Aluminium-Mutter-Legierung, die Chrom enthält, und der restlichen Elemente außer als Aluminium und Chrom oder Mutter-Legierungen der Elemente durch ein mechanisches Legierungsverfahren, einen Schritt zum teilweise oder vollständigen Umwandeln des kristallinen Pulvers in einen amorphen Zustand durch ein thermisches Aktivierungsheizverfahren, und einen Schritt zum Ausführen einer Warmerstarrung des amorphen Pulvers.

8. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 7, worin der amorphe Umwandlungsschritt und der Warmerstarrungsschritt gleichzeitig ausgeführt werden.

9. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 7 oder 8, worin die thermische Aktivierungs-Temperungsbehandlung in einem Temperaturbereich von 400 bis 800 K ausgeführt wird.

10. Verfahren zur Herstellung einer auf Aluminium-Chrom basierenden Legierung nach Anspruch 7, 8 oder 9, worin die Warmerstarrungsbehandlung bei einer Temperatur durchgeführt wird, die höher als der Glasübergangspunkt der amorphen Phase und niedriger als ihre Kristallisationstemperatur ist.

Revendications

1. Alliage à base d'aluminium-chrome contenant de 10 à 25% en rapport atomique de Cr, facultativement au plus 30% en rapport atomique d'au moins un élément choisi parmi Ti, Zr, Si, V, Nb, Mo, W, Mn, Co et Hf, et de 0,1 à 5,0% en rapport atomique d'au moins un élément choisi dans le groupe de Fe et Ni, où

la teneur totale en ledit Cr, et ledit Fe et/ou Ni ne dépasse pas 30% en rapport atomique, et le reste, en-dehors des impuretés, est composé d'aluminium, ledit alliage à base d'aluminium-chrome présentant partiellement ou entièrement une structure amorphe par diffraction de rayons X ou diffraction de faisceaux d'électrons, caractérisé en ce que des matières de renforcement de seconde phase comme des particules, des whiskers et des fibres courtes sont contenues dans des états dispersés.

2. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 1, ledit procédé comprenant:

une étape d'obtention d'une matière première en feuille ou en poudre à partir d'une masse fondue par un procédé de solidification rapide, une étape d'obtention d'une poudre, transformée en un état amorphe, par réalisation d'un traitement de broyage mécanique ou d'un traitement d'usinage mécanique équivalent sur ladite matière première, et une étape de réalisation d'une solidification à chaud de ladite poudre amorphe.

3. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 2, dans lequel ladite poudre de matière première obtenue par ledit procédé de solidification rapide a une structure quasi-cristalline.
4. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 2 ou 3, dans lequel ledit traitement de solidification à chaud est effectué à une température supérieure au point de transition vitreuse de ladite phase amorphe et inférieur à sa température de cristallisation.
5. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 1 comprenant:
 - une étape d'obtention d'une poudre d'alliage de système binaire aluminium-chrome à partir d'une masse fondue d'un alliage de système binaire aluminium-chrome par un procédé de solidification rapide, et une étape d'alliage des éléments restants autres que l'aluminium et le chrome dans ladite poudre d'alliage de système binaire aluminium-chrome par un procédé d'alliage mécanique.
6. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 5, dans lequel ladite poudre d'alliage de système binaire aluminium-chrome obtenue par ledit procédé de solidification rapide a entièrement ou partiellement une structure quasi-cristalline.
7. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 1, comprenant:
 - une étape d'obtention d'une poudre cristalline par alliage d'une poudre d'aluminium de pureté industrielle, de chrome pur ou d'un alliage mère d'aluminium contenant du chrome, et des éléments restants autres que l'aluminium et le chrome ou les alliages mères desdits éléments par un procédé d'alliage mécanique,
 - une étape de transformation partielle ou entière de ladite poudre cristalline en un état amorphe par un procédé de recuit avec activation thermique, et
 - une étape de réalisation d'une solidification à chaud de ladite poudre amorphe.
8. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 7, dans lequel on réalise simultanément ladite étape de conversion amorphe et ladite étape de solidification à chaud.
9. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 7 ou 8, dans lequel ledit traitement de recuit par activation thermique est effectué dans un intervalle de température de 400 à 800 K.
10. Procédé de préparation d'un alliage à base d'aluminium-chrome selon la revendication 7, 8 ou 9, dans lequel on effectue ledit traitement de solidification à chaud à une température supérieure au point de transition vitreuse de ladite phase amorphe et inférieure à sa température de cristallisation.

FIG. 1A

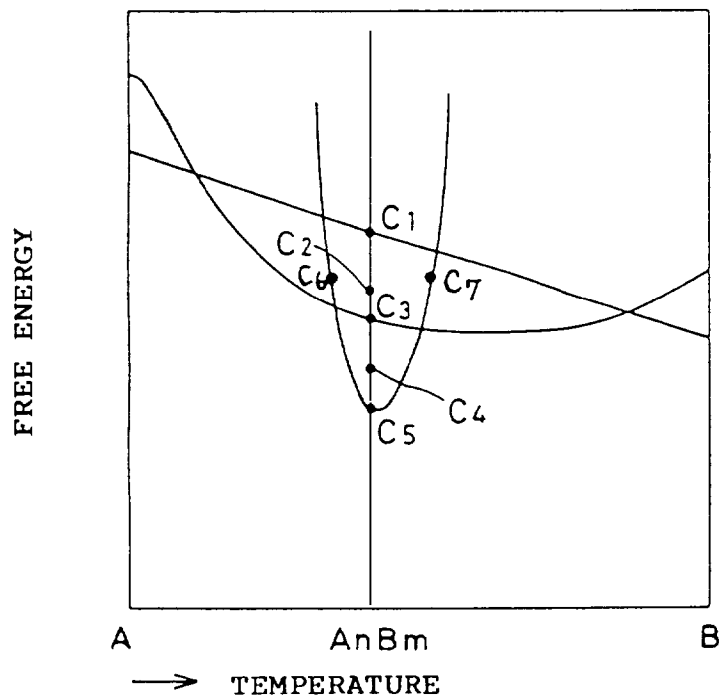


FIG. 1B

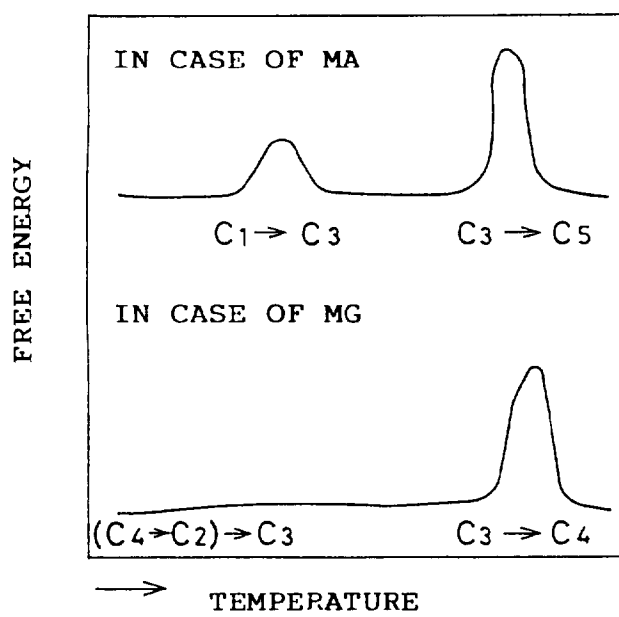


FIG. 2

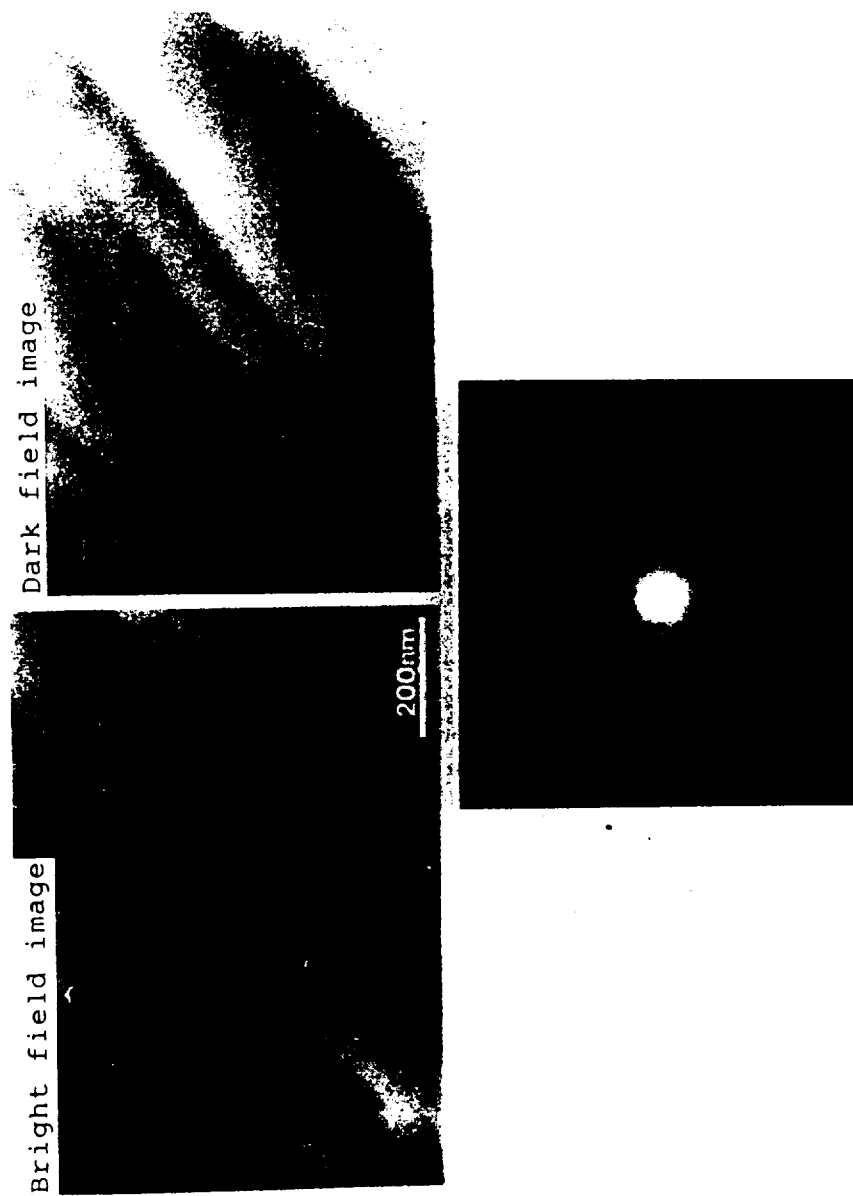


FIG. 3

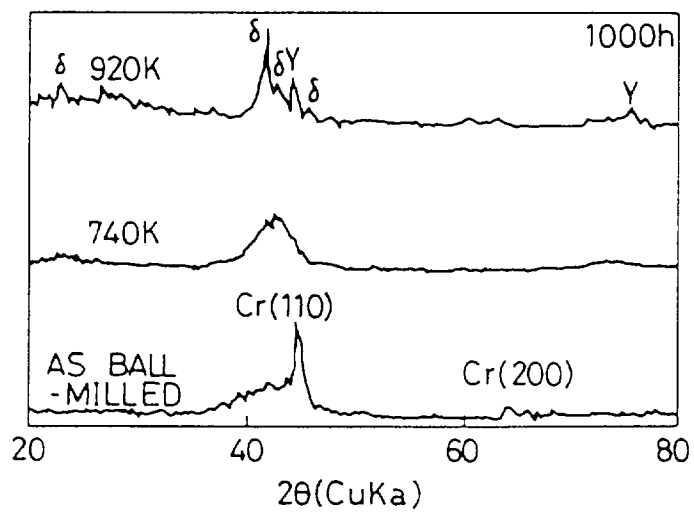


FIG. 4

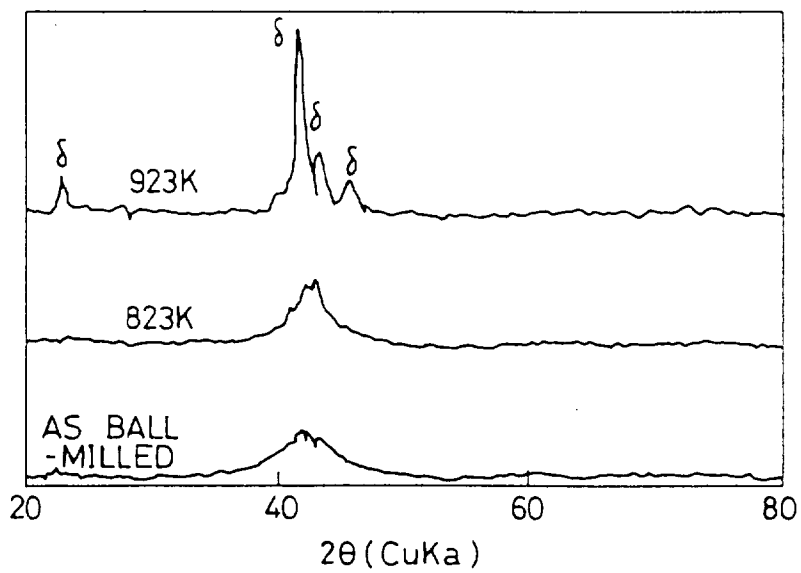


FIG. 5

